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(54) Title: PROCESS FOR SURFACE TREATMENT OF POLYETHYLENE TEREPHTHALATE ARTICLE (57) Abstract There is disclosed herein a process for preparing an oriented polyethylene terephthalate article, by (a) surface treating the article to obtain good adhesive bonding by increasing the concentration of surface polar groups, and then (b) contacting the treated surface with suitable solvent that preserves the good adhesive bonding characteristics but removes undesirable blocking characteristics.		

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TITLE

PROCESS FOR SURFACE TREATMENT OF POLYETHYLENE TEREPHTHALATE ARTICLE

5

BACKGROUND OF THE INVENTION

Polyethylene terephthalate (PET) has been demonstrated as an effective polymer for a wide variety of products. Its properties of strength, durability and the like make it suitable for any number of applications, from filaments and fibers to beverage containers. The preparation of polymeric linear terephthalic esters is disclosed in U.S. 2,465,319 and is incorporated by reference herein. In general this preparation involves the condensation of ethylene glycol and terephthalic acid.

Many uses of polyethylene terephthalate are derived from the film form. Films are prepared by any number of techniques well known to the practitioner, including extrusion. Moreover if the polyethylene terephthalate film is molecularly oriented, certain physical properties such as tensile strength, impact strength, flex life, water vapor, and organic vapor permeability and tensile modulus are enhanced. U.S. 2,823,421 which is incorporated by reference herein, is directed to the stretching of polyethylene terephthalate film to produce an oriented product having an outstanding combination of physical, chemical and electrical properties. An extruded, molten, amorphous film of polyethylene terephthalate is continuously longitudinally stretched at least at the rate of 400 percent per minute no greater than 3.25 times at a temperature of between 80-90°C. The longitudinally stretched film is preheated at between 90-95°C and continuously transversely stretched substantially the same amount of at least 400 percent per minute at a temperature of 90-110°C to

produce a balanced film. The biaxially stretched film is thereafter heat-set at a temperature within the range 150-250°C.

Oriented polyethylene terephthalate is widely used in a variety of industries including electronics (as dielectrics, coverings, and the like), the wire and cable industry (as for example filaments and protective sheaths), fibers, and polymeric articles of manufacture (such as beverage containers), to name a few. It finds particular application in the medical device field, including medical dilatation products where strength is a critical property. For example, U.S. Re 33,561 relates to balloon catheters especially useful in medical dilatation procedures, and is incorporated by reference herein. This patent provides for balloon catheters useful for the relief of arterial stenosis and other ailments requiring a surgical procedure involving insertion of an instrument into blood vessels or body cavities. These balloons are effective in that they have thin walls which are flexible and readily collapsible and easily transportable within the body. Other physical properties include minimal radial expansion on inflation, and high burst strength (and rupture if at all in the axial direction to ensure against a traumatic removal), among other attributes making these balloons effective for a number of medical procedures. The patent requires that the flexible balloon be made of a high molecular weight, biaxially oriented polymer having a burst pressure of at least 200 psi (1.4 MPa) and a radial expansion of less than 5 percent at 200 psi (1.4 MPa).

One limitation to oriented polyethylene terephthalate film is that it is difficult to adhesively bond to other polymeric substrates. Such adhesion is desirable as with Re 33,561 inasmuch as the polymeric

balloon must be suitably attached to other medical instruments for insertion into a vessel and surgical manipulation. The surface adhesion properties of oriented polyethylene terephthalate film are improved when it is subjected to a surface treatment. Such treatments include, for example, subjecting the film to any of the following: electrical stress accompanied by corona discharge; a flame; a gaseous plasma (such as oxygen, chlorine, etc.); short wave ultraviolet light; and oxidizing chemicals (sulfuric acid-dichromate, potassium permanganate, etc.). The treated surface is generally characterized by measuring the contact angle between a drop of liquid (usually water) and the treated surface, according to conventional techniques. For example, the Sessile drop technique as reviewed by R. E. Johnson, Jr. and R. H. Dettre, "Surface and Colloid Science", Volume 2, Interscience, New York, NY, 1969 measures advancing and receding contact angles for two chemicals at a given temperature. High contact angle values indicate a low concentration of polar groups (or less adhesion) and low values indicate a high concentration of polar groups (or more adhesion).

However, a consequence of such treatment procedures is that the oriented polyethylene terephthalate film undesirably adheres to itself when two such treated surfaces are in contact with one another. This phenomenon is known as blocking, and can occur when surfaces are stacked for storage, when folds of dilatation balloons are tightly wrapped together, when filaments are pinched together, and many other situations. The blocking tendency is enhanced under high humidity conditions and moderate pressure during storage. Although blocking is known to occur in untreated oriented polyethylene terephthalate articles, this occurs under extreme conditions of temperature and

pressure. Other factors contributing to blocking are those treatments necessary for enhanced adhesion to other materials. Blocking can be so severe that when the surfaces are pulled apart, damage is so extensive as
5 to render the article unusable.

D. K. Owens, in "Journal of Applied Polymer Science", 19, 3315 (1975) has shown that oriented polyethylene terephthalate film exhibits self-adhesion (bonding under heat and pressure) after corona or short-
10 wave ultraviolet radiation. Owens found that bond strength could be greatly reduced by the application of hydrogen bonding liquids to the surface, but the self-adhesion returned when the liquids were removed. Owens also showed that self-adhesion could be reduced by
15 chemical reaction of the polar groups on the treated surface using acetyl chloride, nitric acid, sodium hydroxide and sodium carbonate.

It would be desirable, therefore, to contact a treated oriented polyethylene terephthalate surface with
20 a non-reactive solvent to that the surface could be bonded with adhesives but not exhibit unacceptable blocking.

SUMMARY OF THE INVENTION

There is disclosed and claimed herein a process for
25 the preparation of an article of oriented polyethylene terephthalate exhibiting low self-adhesion and high bondability to other surfaces, comprising:

- (a) treating an article on the surface thereof and subsequently
- 30 (b) contacting the surface thereof with solvent.

In this process the article of oriented polyethylene terephthalate has an initial polarity associated with it. The surface treatment (a) increases
35 the polarity and further the solvent contact (b)

decreases the polarity resulting from (a). The net effect of steps (a) and (b) is that the polarity of the polyethylene terephthalate is increased relative to the initial polarity.

5 A wide variety of articles of manufacture are contemplated for preparation according to the process of the invention. Films and tubes made be prepared by this process, with the size and shape to be selected according to the needs of the practitioner. In the
10 previously referenced field of medical devices, medical dilatation balloons are advantageously prepared according to Re 33,561 and using oriented polyethylene terephthalate film with enhanced properties according to the presently disclosed process.

15 DETAILED DESCRIPTION OF THE INVENTION

Polyethylene terephthalate is prepared by any of a number of techniques; one such procedure is according to U.S. 2,465,319. The resulting product in the form of a film is next stretched in longitudinal and transverse
20 directions in a manner such as is described in U.S. 2,823,421 to derive a biaxially oriented polyethylene terephthalate film.

In the surface treatment step (a), "surface" is any of the surfaces of the article for which enhanced
25 properties according to this invention is desired. It may be one side of the article or for example the inside and outside of a dilatation balloon. The surface treatment may be selected from a wide variety of conventional techniques, including without limitation
30 electrical stress accompanied by corona treatment; plasma treatment; flame treatment; ultraviolet light treatment; and chemical treatment.

Corona treatment and ultraviolet light treatment can be conducted according to the procedures set forth
35 in Owens, D. K., "The Mechanism of Corona and

Ultraviolet Light Induced Self-Adhesion of Poly(ethylene terephthalate) Film", Journal of Applied Polymer Science, Vol. 19, pp. 3315-3326 (1975). Corona treatment is also described in Owens, D. K., "Mechanism of Corona-Induced Self-Adhesion of Polyethylene Film", Journal of Applied Polymer Science, Vol. 19, pp. 265-271 (1975).

A discussion of surface treatment using plasma is found in Rose, P. W. and Kaplon, S. L., "Plasma Treatment", Plastics Finishing and Decoration, Van Nostrand Reinhold Company, 1986. Preferably, surface treatment using plasma is conducted for less than about 16 minutes and at less than 300 watts. U.S. 3,431,435 and U.S. 3,153,683 review the fundamentals of flame treatment. Any of a variety of chemicals may be utilized for their surface treating properties. Such chemicals are selected according to desired result, as is readily appreciated by those skilled in the art.

With respect to the solvent contact step (b) and without intending to limit the generality of the foregoing, suitable solvents for contact with the surface of the polyethylene terephthalate include ketones, alcohols, and esters, each of these categories having from 3 to 12 carbon atoms (branched or linear), amides having from 2 to 12 carbon atoms (branched or linear), chloroform, and carbon disulphide. More preferred solvents from this group are isopropanol, acetone, carbon disulphide, chloroform, cyclohexanol, and formamide. Our research indicates that acetone is the most preferred solvent.

According to the process of the invention and using acetone as the preferred solvent, the biaxially oriented polyethylene terephthalate is contacted with acetone for a period of at least about 1 minute, at ambient temperature. From the moment of application of room

temperature acetone through about the first 5 minutes, there is a reduction in surface blocking observable. From about 5 minutes to about 10 minutes this effect is measurable. From about 10 to about 30 minutes there is
5 observed an increased alteration of surface polarity, and during the ensuing period from about 30 to about 60 minutes still further reduction of blocking is observable. The period of from about 60 minutes to about 120 minutes after application of the acetone is
10 considered to achieve the maximum effective increase in surface polarity, and after this interval there is a tendency for blocking to increase. These observations on blocking are highly indicative of surface polarity characteristics, in that polar groups responsible for
15 blocking are being removed.

After application of the solvent to the surface of the polyethylene terephthalate article for the desired period of time, the solvent is removed. The treatment is effective with some solvent present on the article
20 after removal, so that substantially all of the solvent is removed. Removal may be by air drying for a suitable period of time or by other methods, including partial reclamation of the solvent.

In addition to observations on polarity, another
25 means to define the invention claimed herein is to measure polar and dispersive surface tensions of the article. This may be done by other methods readily understood by those skilled in the art. Using the surface tension approach, the process involves first
30 forming the article of biaxially oriented polyethylene terephthalate having a ratio of the polar surface tension to the dispersive surface tension usually about 0.25. The article is next treated on a surface by exposure to an ionizing energy source (e.g., plasma)
35 such that the ratio is greater than about 0.7. The

article is then contacted with a solvent such that the ratio is decreased relative to that observed after surface treatment but increased to that observed for the untreated article. Substantially all of the solvent is
5 then removed.

EXAMPLES

COMPARATIVE EXAMPLE 1

A biaxially oriented polyethylene terephthalate (OPET) film was prepared by extruding polyethylene
10 terephthalate polymer having an intrinsic viscosity of about 1.0 into film having a thickness of 0.23 mm at a temperature of 280°C by conventional means and then biaxially orienting the extruded film 3 times the
15 original length in the machine direction and 4 times the original length in the transverse direction using a T. M. Long Laboratory Film Stretcher at a temperature between 90 and 95°C. The OPET film was then heat set by clamping the film between frames to prevent shrinking, and then heated at 180°C for 1 minute in a hot air oven.
20 The surface of the film was then plasma treated in an oxygen atmosphere for 8 minutes at 300 watts. A drop of deionized water was placed on the treated surface at one end of a 1 inch by 2 inch strip of film, which was then folded lengthwise so that the treated surfaces were
25 facing each other with a layer of water between them. The water promotes the tendency of the material to block insofar as it accelerate hydrogen bonding at high humidity conditions. The folded sample was allowed to sit overnight (about 16 hours). Attempts to separate
30 the folded film resulted in tearing and delamination indicating severe blocking of the surfaces.

COMPARATIVE EXAMPLE 2

A sample of heat set OPET film prepared as in Comparative Example 1, but not plasma treated, did not
35 exhibit blocking after being wet with water as above.

No surface damage was observed when the film surfaces were separated.

EXAMPLE 1

The treated surface of the plasma treated film of Comparative Example 1 was washed with acetone and allowed to dry in air. A drop of deionized water was placed on the treated surface and then the film was folded so that the treated surfaces were facing each other with a layer of water between the surfaces. Plasma treated films that were not washed with acetone were prepared in a similar manner. After an hour of contact time the unwashed film samples had blocked surfaces while the acetone washed sample could be separated without tearing and delamination.

COMPARATIVE EXAMPLE 3

The plasma treated film of Comparative Example 1 which was washed with methanol was found to have blocked surfaces after following the procedure in Example 1.

EXAMPLE 2

PET resin having an intrinsic viscosity of 1.05, a density of 1.41 g/cm³ and a diethylene glycol content of 1.8 weight percent was dried to less than 0.005 weight percent water at 177°C and then processed into single lumen tubing having an outside diameter of 0.34 mm and a wall thickness of 0.064 mm using conventional tubing extrusion techniques.

Biaxially oriented balloons having an outside diameter of 3 mm, a single wall thickness of 0.0076 mm and a cylindrical length of 2 cm were fabricated from the extruded tubing using the process of U.S. Patent No. Re. 33,561 and then plasma treated in an oxygen atmosphere maintained at a pressure about 33.33 Pa in a Gasonics/IPC model 4155/2 plasma treater for 16 minutes at 300 watts and 13.56 MHz.

Within one hour after plasma treatment, seven balloons were placed in a glass container containing about 80 ml of acetone having a purity of 99.9% so that all surfaces of the balloons were completely contacted with the acetone inside and outside. A glass cover was placed over the container. After a one minute soak time the cover was removed and the balloons were taken out individually. Excess acetone was removed from the inside surfaces by wicking followed by an argon gas purge.

The balloons were tested for blocking by connecting the proximal end of a balloon to a Tuohy-Borst adapter and then heat sealing the distal end with an electrical heating element. The Tuohy-Borst adapter with the sealed balloon attached was then connected to a "PRESTO" inflation device of C. R. Bard, Inc. (USCI Division), that had been deaerated as much as possible and contained 4 cm³ of distilled water. With the inflation device pointed down, the plunger was pulled to its limit to remove the air from the balloon while evacuating the balloon to a pressure of about 16 KPa. With the air out of the balloon the screw plunger was pushed and rotated to achieve a pressure of 1300 KPa. This pressure was held for one minute while the balloon was checked for leaks. If no leaks were found, the plunger was pulled to its limit, again with the pressure device pointing down, to achieve a balloon pressure of about 16 KPa. While ensuring that the balloon had been completely deflated, this pressure was held for 20 minutes. The balloon was then inflated to a pressure of 1200 KPa as quickly as possible and maintained at that pressure for one minute while the balloon was checked for leaks. The balloon pressure was returned to atmospheric and the Tuohy-Borst adapter and balloon were disconnected from the inflation device. The balloon inside surface was

then examined for delamination caused by blocking using a stereo polarizing microscope. Changes in balloon wall thickness as a result of delamination were evident as localized differences in retardation colors when viewed
5 between crossed polaroids.

The Tuohy-Borst adapter with balloon was reattached to the inflation device and the vacuum - pressure - vacuum cycle was repeated except that the final vacuum was held for 40 minutes. The balloon was again checked
10 for leaks at 1200 KPa and reinspected for delamination using the stereo polarizing microscope.

The vacuum - pressure - vacuum cycle was repeated again except that the final vacuum was held for 140 minutes. Checks for leaks and delamination were
15 repeated.

None of the seven balloons had leaks or showed evidence of blocking when examined under the stereo polarizing microscope.

COMPARATIVE EXAMPLE 4

20 Three balloons fabricated and plasma treated as in Example 2, but not subjected to acetone washing, had leaks and showed evidence of delamination after the first 20 minute vacuum - pressure - vacuum cycle test procedure described in Example 2.

25 EXAMPLE 3

Four balloons were plasma treated and submerged in acetone as were described in Example 2 but processed in the following manner:

(A) As fabricated.

30 (B) As fabricated plus a 90 minute acetone soak followed by individual removal and wicking of excess acetone. The balloons were then placed into a covered glass petri dish, and into an evacuated room temperature vacuum chamber at a pressure of 3.3 Pa for about 10
35 minutes. The vacuum chamber was brought to atmospheric

pressure with nitrogen, and petri dishes containing balloons were removed.

(C) As fabricated plus plasma treatment.

(D) As fabricated plus plasma treatment followed by a 90 minute acetone soak and acetone removal process as described in (B).

Contact angles for the balloons are first measured according to the Sessile Drop technique, as is readily practiced by those skilled in the art. Subsequent to this measurement, the dispersion surface tension (DST) and the polar surface tension (PST) were calculated for the inner balloon surfaces (Table 1) using the Harmonic-Mean Method described in Souhang Wu's book "Polymer Interface and Adhesion", Marcel Dekker, Inc., p. 178 (1982).

Table 1

<u>Balloon Type</u>	<u>DST, dyne/cm</u>	<u>PST, dyne/cm</u>	<u>PST/DST</u>
A	34.5	8.5	0.25
B	35.3	7.9	0.22
C	31.1	23.9	0.77
D	31.7	18.8	0.59

Table 1 shows acetone washing has little or no effect on the polar surface tension of the inner surface of non-plasma treated balloons and a significant effect (reduction) on the polar surface tension of plasma treated balloons.

EXAMPLE 4

The inside surfaces of the four balloons processed in the same manner as Example 3 were analyzed for surface element content using a Perkin Elmer PHI 5000 Electron Spectrometer for Chemical Analysis (ESCA) instrument. The results (Table 2) show that plasma treatment increases the polar group concentration on the

- surface and that plasma treatment followed by an acetone wash removes some of the polar groups, but not to the level of the untreated surface. The remaining polar groups on the inside surface of Type D balloons are
- 5 sufficient to provide good adhesive strength, but do not contribute to blocking.

Table 2

ESCA Analysis Results

<u>Balloon Type</u>	<u>C, %</u>	<u>O, %</u>	<u>N, %</u>	<u>O/C</u>
A	71	29	0	0.41
B	71	29	0	0.41
C	62	37	0.9	0.60
D	68	33	0	0.49

EXAMPLE 5

- 10 Ten Type D balloons were bonded to polyethylene catheters that had been solvent washed and plasma treated in the manner described above, with an ultraviolet curable adhesive in a manner as is readily appreciable by one skilled in the art. The balloon-
- 15 catheter assembly was then tested to failure by increasing the fluid pressure in the balloons with the Presto inflation device until a leak was observed. All of the failures occurred in the balloon wall (as opposed to at the adhesive joint) indicating good adhesive bond
- 20 strength between the polyethylene catheters and the PET balloon surfaces.

EXAMPLE 6

- Samples of the plasma treated films of Comparative Example 1 were washed, each with a different solvent
- 25 (Table 3), dried in a vacuum oven at room temperature at a pressure of about 13 KPa for 16 hours and then tested for blocking as in Comparative Example 1.

Table 3

<u>Solvent</u>	<u>Blocking Observed</u>
Carbon Disulfide	No
Chloroform	No
Cyclohexanol	No
Ethanol	Yes
Ethyl Acetate	Yes
Formamide	No
Hexane	Yes
Isopropanol	No
Methylene Chloride	Yes
Toluene	Yes

EXAMPLE 7

Five balloons were fabricated, plasma treated, and acetone washed as in Example 2, except that the acetone soak time was 5 minutes. Three of the balloons did not leak or show evidence of delamination after the described 140 minute period. The remaining two balloons leaked and showed evidence of delamination after the 140 minute period; this is probably due to variability in wall thickness and/or surface characteristics of these samples.

COMPARATIVE EXAMPLE 5

Five balloons were fabricated and plasma treated as in Example 2, but not subjected to acetone washing. Four of these balloons leaked and showed evidence of delamination after the first 20 minute cycle test procedure. One balloon did not leak or delaminate until the 140 minute test procedure; this is probably due to variability in wall thickness and/or surface characteristics of this sample.

EXAMPLE 8

Many factors contribute to the blocking phenomenon of biaxially oriented PET (including treatment level, surface texture, molecular orientation level and contact pressure and time). Likewise, there are many variables involved in reducing blocking tendency by solvent washing (including solvent type, contact time and temperature). The objective of the following series of experiments is to determine the important variables and the magnitude of their effect on blocking.

In this experiment there were 18 runs involving plasma treatment levels, three solvents, three solvent contact times and temperatures. The balloons were made as in Example 2, except the PET resin had an intrinsic viscosity of 1.03 and a diethylene glycol content of 1.9 weight percent. Plasma treatment was conducted as described in Example 2 but with the following exceptions. The plasma treatment levels were 0 = none, -1 = low (100 watts for 3 minutes at an oxygen pressure of 33 Pa.) and 1 = high (300 watts for 17.5 minutes at an oxygen pressure of 13 Pa.). "High" is approximately seven times greater than "low". The three solvents were 0 = ethanol (solubility parameter (SP) = 12.7), -1 = acetone (SP = 10.0) and 1 = isopropyl alcohol (SP = 11.6). The solvent contact times were 30, 90 and 270 minutes and the solvent temperatures were 24, 38 and 51°C. After plasma treatment, solvent contact and solvent removal as described in Example 3 (B), the ratio of the polar surface tension (PST) to dispersive surface tension (DST) of the inside surfaces of the balloons were measured as also described in Example 3. The experimental design runs and PST/DST ratios are given in Table 4.

Table 4

<u>Run No.</u>	<u>Plasma</u>	<u>Solvent</u>	<u>Temp. (C)</u>	<u>Time, min</u>	<u>PST/DST</u>
1	0	-1	38	90	0.24
2	1	1	24	30	0.38
3	1	0	38	30	0.64
4	-1	1	51	270	0.60
5	-1	-1	51	270	0.40
6	-1	-1	24	30	0.62
7	0	0	24	30	0.32
8	1	-1	24	90	0.55
9	0	1	51	30	0.30
10	-1	1	24	270	0.67
11	1	-1	51	30	0.48
12	1	0	51	90	0.60
13	1	-1	51	270	0.54
14	-1	-1	51	30	0.45
15	-1	-1	24	270	0.46
16	-1	1	38	30	0.53
17	1	0	24	270	0.61
18	1	1	51	270	0.65

A multiple regression analysis of the data was made. The PST/DST ratio was correlated with plasma treatment levels and the solubility parameters of the solvent. The results show that plasma treatment level and solvent (solubility parameter) multiplied by the contact time (SxT) have the most significant effect on the PST/DST ratio. The PST/DST ratio increases with increasing treatment level and increasing SxT.

EXAMPLE 9

In this experiment there were 14 runs with 5 replicates for each run to study the effect of the variables, solvent type, plasma treatment level and solvent contact time on blocking. The balloons were prepared as described in Example 3 (B) and the solvents

and plasma treatment levels were also the same as in Example 8. The balloons were tested for blocking using the method described in Example 2. A blocking tendency value was determined for each run by assigning a value of 20 to balloons that failed after 20 minutes, 10 to balloons that failed after 40 minutes, 2 to balloons that failed after 140 minutes and 0 to balloons that did not fail after 140 minutes. The blocking tendency for a given run was the sum of the blocking tendency of the 5 replicates in the run. The experimental design runs and the blocking tendency values are given in Table 5.

Table 5				
<u>Run No.</u>	<u>Plasma</u>	<u>Solvent</u>	<u>Time, min</u>	<u>Blocking Tendency</u>
1	-1	-1	270	62
2	1	1	270	100
3	1	0	30	60
4	1	-1	270	90
5	-1	0	270	42
6	0	-1	30	0
7	-1	-1	150	70
8	0	1	150	0
9	-1	1	30	70
10	0	0	270	0
11	1	0	150	100
12	1	-1	30	42
13	0	none	0	0
14	0	none	0	0

A multiple regression analysis of the data in Table 5 was performed using the same method as for the data in Table 4. The results show that increasing plasma treatment level has a very strong effect in increasing blocking tendency. The effect of plasma treatment on blocking tendency is moderated by contact with solvents

having a solubility parameter within about 2 units of the solubility parameter of PET.

What is claimed is:

1. A process for the preparation of an article of oriented polyethylene terephthalate exhibiting low self-adhesion and high bondability to other surfaces,
5 comprising:

(a) treating an article on the surface thereof and subsequently
(b) contacting the surface thereof with solvent.

- 10 2. The process of Claim 1 wherein the article of oriented polyethylene terephthalate has an initial polarity associated therewith, and the surface treatment
(a) increases the polarity and further the solvent contact (b) decreases the polarity resulting from (a),
15 so that the polarity of the polyethylene terephthalate after the surface treatment (a) and the solvent contact (b) is increased relative to the initial polarity.

3. The process of Claim 1 wherein the surface treatment (a) is selected from the group consisting of
20 electrical stress accompanied by corona treatment, plasma treatment, flame treatment, ultraviolet light treatment, and chemical treatment.

4. The process of Claim 3 wherein the surface treatment (a) is plasma treatment.

- 25 5. The process of Claim 4 wherein plasma treatment is conducted for less than about 16 minutes and at less than about 300 watts.

6. The process of Claim 1 wherein the solvent in (b) is selected from the group consisting of ketones,
30 alcohols, and esters having from 3 to 12 carbons, amides having from 2 to 12 carbons, chloroform, and carbon disulphide.

7. The process of Claim 6 wherein the solvent in (b) is selected from the group consisting of

isopropanol, acetone, carbon disulphide, chloroform, cyclohexanol, and formamide.

8. The process of Claim 1 wherein the polyethylene terephthalate is biaxially oriented.

5 9. The process of Claim 8 wherein solvent contact (b) further comprises contacting the biaxially oriented polyethylene terephthalate with acetone for a period of at least about 1 minute, at ambient temperature.

10 10. The process of Claim 9 wherein solvent contact (b) further comprises contacting the biaxially oriented polyethylene terephthalate with acetone for a period of from about 60 minutes to about 120 minutes, at ambient temperature.

15 11. The process of Claim 1 wherein substantially all of the solvent in (b) is removed after contact with the surface of the article.

12. A process for the preparation of an article of polyethylene terephthalate exhibiting low self-adhesion and high bondability to other surfaces, comprising:

20 (a) forming an article of biaxially oriented polyethylene terephthalate, said article having a ratio of a polar surface tension to a dispersive surface tension of about 0.25;

25 (b) treating said article on a surface thereof by exposure to an ionizing energy source such that the ratio of the polar surface tension to the dispersive surface tension is greater than about 0.7;

(c) contacting said article after treatment (b) with a solvent such that the ratio is decreased from the ratio of (b) and increased from the ratio of (a);
30 and

(d) removing substantially all of said solvent of (c).

35 13. A film prepared according to the process of Claim 1.

14. A tube prepared according to the process of Claim 1.

15. A medical dilatation balloon prepared according to the process of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/07761

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08J7/00 C08J7/02 //A61L29/00, C08L67:02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08J A61L

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-096840[12] & JP,A,5 039 374 (DAINIPPON PRINTING CO. LTD.) 19 February 1993 see abstract	1-4,6,7, 12,13
X	GB,A,2 083 049 (SHIN-ETSU CHEMICAL CO.) 17 March 1982 see claims 1,2,10,13,14 see examples 16,17; tables 4,5 see page 2, line 10 - line 17 see page 2, line 34 - line 37	1,3,4,6, 7,13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 December 1993

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/ 3/07761

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 868 006 (YORKGITIS E. ET AL) 19 September 1989 see claims 1,3,5,9,11 see column 15, line 20 - line 59 see column 16, line 18 - line 23 see column 16, line 62 - column 17, line 15 see example 9	1,3,6-9, 13
A	US,H,688 (SOBATAKA W.S. ET AL) 3 October 1989 see claims 1,5,7,8,12	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 93/07761

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		JP-A- 57049627	23-03-82
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US-H-688	03-10-89	NONE	